



Effect of TiO₂ on Pt-Ru-based anodes for methanol electroreforming

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ABSTRACT

This study examines the electrochemical reforming of methanol for hydrogen production using novel DSA type anodes (modified with TiO₂) with low metal loadings. Mass spectrometry (MS) in conjunction with electrochemical techniques were used to study the performance of the process as well as crossover phenomena. The electrolysis process was carried out in a Polymer Electrode Membrane (PEM) electrolyzer comprised of a Pt-Ru modified with TiO₂ anode, a commercial Pt/C cathode, and a Nafion 117 electrolyte. Both methanol concentration and cell temperature were varied to investigate the cell performance. In all cases, our results showed that the Pt-Ru-TiO₂ electrode had better electro-catalytic activity than the Pt-Ru electrode. This higher electro-catalytic activity of the TiO₂-modified electrode was attributed to the enhanced Pt-Ru dispersion as well as the formation of smaller Pt and Ru particles, and thus to the higher electrochemical active surface. For all studied Membrane Electrodes Assemblies (MEAs), both CO₂ and methanol crossover were observed at the cathode of the cell. In addition, it was found that hydrogen production is taking place with Faradaic efficiency values very close to 100%. This study demonstrates that the TiO₂-modified electrode with a decreased noble-metal loading can increase the current density up to 56%.

1. Introduction

The improvement of life quality is an important issue in modern society. However, this issue is closely related to energy consumption. Currently, the main source of energy comes from fossil fuel. With that in mind, the dramatic decrease of fossil fuel and increase of environmental problems such as air pollution and climatic change, have led to alternative ways of clean and sustainable energy production [1]. The utilization of hydrogen (H₂) as a clean fuel for combustion engines or fuel cells has been proposed for this purpose [2]. Hydrogen is among the most abundant elements on earth. Though hydrogen is present in many substances, it requires additional processing to be usable. Thus, hydrogen is not considered as an energy source but as an energy carrier.

It can be produced using various methods, each one with advantages and disadvantages. At present, steam reforming of fossil fuel is the dominant route leading up to 96% of hydrogen production [3,4]. Steam reforming is also the most cost-effective method for a large scale hydrogen production [5,6]. These processes suffer from many drawbacks such as co-production of carbon dioxide and the use of non-renewable energy sources. Electrolysis is the best alternative technique for high pure hydrogen production in a rapid and simple way. An excellent candidate process for pure hydrogen production tends to be water electrolysis [7]. Unfortunately, this process is economically undesirable mainly due to the high overpotential in catalytic anode where

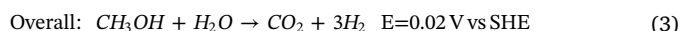
the oxygen evolution reaction takes place subsequent to the high-energy consumption. It has been reported that the energy consumption for water electrolysis is 39.4 kW h kg⁻¹ or 3.54 kW h Nm⁻³ of hydrogen and for a commercial electrolyzer it is about 50–55 kW h kg⁻¹ or 4.5–5 kW h Nm⁻³ of hydrogen [8].

The hydrogen production from methanol electrolysis is the most promising approach. The success of this method depends on the low operating potential that can accomplish the hydrogen production (0.02 V vs SHE), compared to water electrolysis (1.23 V under standard conditions) [9,10]. Methanol can be economically mass-produced mainly by synthesis gas process [11]. A gas mixture of hydrogen and carbon monoxide, known as synthesis gas (syngas) is the basis for almost all methanol production pathways today. Another route for hydrogen production is via renewable resources such as biomass. It is important to consider that methanol electro-reforming can take place even at ambient temperature and pressure. The electro-reforming of methanol is not a spontaneous reaction, so the supplying of electric power (DC) is fundamental for the splitting of chemically-bonded species. Methanol is electro-oxidized via a dehydrogenation step to produce mainly carbon dioxide (CO₂), protons (H⁺) and electrons (e⁻) at the anode of a PEM electrolytic cell. Due to the applied potential, the produced protons are transferred to the cathode through the conducting membrane [12,13]. Methanol has been the first and the most studied alcohol for hydrogen production because of its good reactivity and

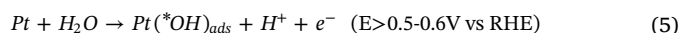
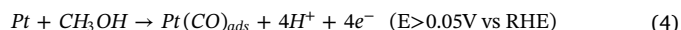
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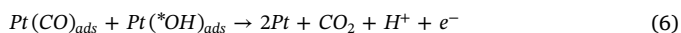
simplicity. However, methanol has high toxicity and solubility in water, and this can lead to environmental hazards. Besides that, other serious disadvantages of methanol electrolysis are the slow kinetics of the anodic methanol electro-oxidation, the loss of fuel due to methanol crossover, as well as the corrosion and poison of the Pt containing anode [14]. The anodic, cathodic, as well as the overall reaction described by Eqs. (1)–(3):



During methanol electro-oxidation, two different reactions can take place at the anodic electrode: 1) the dehydrogenation of methanol to carbon monoxide (Eq. (4)) and 2) the dehydrogenation of water to hydroxyls (OH^-) (Eq. (5)).



The first step (Eq. (4)) leading to the Pt–CO bond starts from low potentials (0.05 V vs RHE) and leads to the active catalyst surface poisoning. The removal of the CO adsorbed species at ambient temperature can be achieved via hydroxyl radicals (based on a Langmuir-Hinshelwood mechanism [15]) according to Eq. (6):



Due to the insufficient activity of pure Pt for methanol oxidation, many studies have been focused on Pt modification using other metals. Addition of a second metal to Pt-catalyst (Pt-M or Pt-MOX, M = Co, Ru, Sn, Ti, Ir, etc) tends to improve the drawback of carbon monoxide poisoning. The state of the art and the most thoroughly investigated catalysts in literature are Pt-Ru-based catalysts deposited mainly on carbon supports [16–21]. The main role of Ru is to offer the active sites for water oxidation at lower potentials. The bi-functional mechanism depends on the operating temperature and potential. For low potentials (below 0.4 V), Pt is the best catalyst for methanol oxidation, but not for water dissociation. On the other hand, Ru is capable of dissociating water at lower potentials. At higher temperatures (above 60 °C), Ru can adsorb methanol and Pt can dissociate water at higher potentials [22–24]. Despite their effectiveness, the high cost of these electrodes is one of the major drawbacks for their further commercialization. Previous studies report that TiO_2 can be used to modify Pt or Pt-Ru electrodes in an effective way without any activity loss [19,20]. Metal-based electrodes modified with TiO_2 are considered advantageous to use due to their cost effectiveness and acid stability [17,25,26]. In addition, Pt and/or Ru nanoparticles can create a uniform dispersion in the presence of TiO_2 . In the literature, there are also reports where titania can be used effectively as a substrate for metal deposition [27,28]. Recently, Chen et al. [28], reported the performance of a novel anodic electrode consisted of Pd nanoparticles deposited on a three-dimensional architecture of titania nanotubes during electro-reforming of biomass in an alkaline electrolyte membrane cell. During this study, Pt-Ru catalysts modified with TiO_2 were deposited on a Ti foam instead of classical carbon-based supports as it can act both as a current collector and a liquid/gas diffusion layer. In addition, Ti foam can offer an extra flow field for methanol fuel maintaining its stability in the strong corrosive environment prevalent within the fuel cell. Pt-Ru binary and Pt-Ru- TiO_2 ternary electrodes with metal loadings of $1.3 \pm 0.1 \text{ mg cm}^{-2}$ were prepared and studied as anodes for methanol electro-reforming.

2. Experimental

The Pt-Ru and Pt-Ru- TiO_2 anodes were prepared by thermal decomposition of chloride precursors (H_2PtCl_6 , RuCl_3 and TiCl_3 Sigma

Aldrich) on Ti foam substrates at high temperature following the preparation method of DSA type electrodes [29–31]. According to previous reports, the above procedure results in Pt deposition yield equal to 60% and that of Ru and TiO_2 equal to 100% [29,30,32,33]. Appropriate ratios of the precursor solutions were selected in order to obtain molar ratio of Pt-Ru and Pt-Ru- TiO_2 equal to 50%–50% and 25%–25%–50% respectively. Every sample was heated first at 70 °C for 10 min followed by calcination at 500 °C for 10 min. This procedure was repeated several times until a final specific mass of $1.3 \pm 0.1 \text{ mg cm}^{-2}$ was reached. The samples were finally calcinated at 500 °C for 60 min.

The homemade Pt-Ru and Pt-Ru- TiO_2 anodes were characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) before the preparation of the MEA. The XRD measurements were carried out by the use of Siemens D-5000 XRD instrument equipped with a Cu K α lamp ($\lambda = 0.15418 \text{ nm}$). The angle range of the X-ray (2θ) was from 10° to 80° at a scan rate of 0.01°/s. The crystallite size calculation was based on the X-ray line broadening of the diffraction peak according to Scherrer's equation [31]. The morphology of the surface was explored with a field emission environmental scanning electron microscope, FE-SEM (FEI QUANTA 250 FEG). The specific surface area (S_{BET}) of the samples were determined from the adsorption isotherms of nitrogen at –196 °C using a TriStar 3000 Micromeritics instrument. Prior to the measurements, the samples were outgassed at 120 °C for 1 h, under N_2 flow.

Nafion 117 membrane (DuPont) was used as a proton conductor electrolyte with a nominal thickness of 178 μm . According to the standard procedure of preparation, the membrane was treated twice for 60 min in a 0.1 M H_2O_2 solution in H_2O at 80 °C, 120 min in 0.1 M H_2SO_4 solution in H_2O at 80 °C, again 120 min in a 0.1 M H_2O_2 solution in H_2O at 80 °C and finally 60 min in H_2O at 80 °C. After each treatment, the membrane was rinsed in H_2O to remove traces of H_2O_2 . For the preparation of the Membrane Electrode Assembly (MEA), anodic electrode (Pt-Ru and Pt-Ru- TiO_2), Nafion 117 and Pt/C (ETEK) were hot pressed at a pressure of 1 metric ton (Fig. 1). The geometrical area of each electrode was 5.29 cm^2 . A piece of carbon cloth was placed on top of the anode (in case of Pt-Ru and Pt-Ru- TiO_2) in order to act as an extra GDL and current collector. Previous experiments (not shown here) showed that the performance of MEAs without this layer of carbon cloth was small and unstable.

Different concentrations of methanol-water solutions were prepared by diluting methanol with 3-D water. These solutions supplied at the

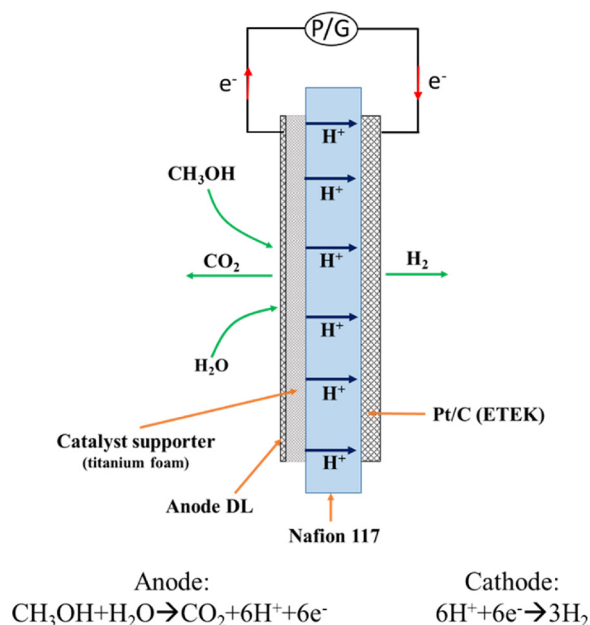


Fig. 1. Schematic diagram of MEA for methanol electrolysis.

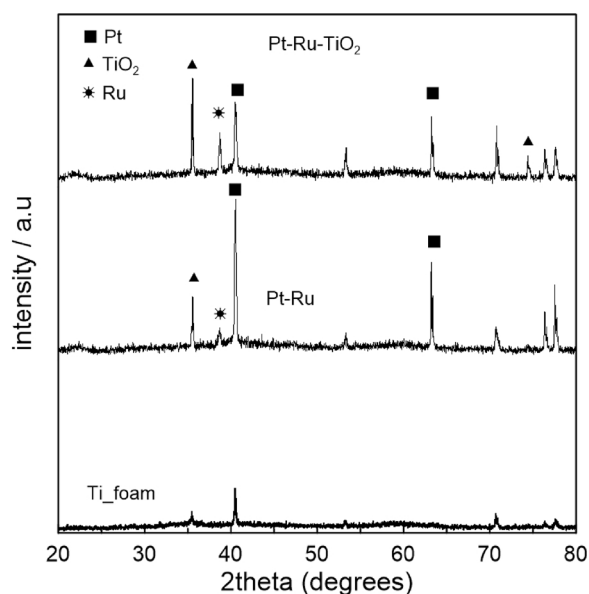


Fig. 2. XRD patterns of the Ti substrate, Pt-Ru and the Pt-Ru-TiO₂ samples.

anodic compartment of the cell with a flow rate of 5 cc/min using a peristaltic pump. A potentiostat/galvanostat (Autolab 302N) was used for positive potential applications across the two electrodes of the electrolyzer. The cathode exhaust gas was analyzed online by a mass spectrometer (Extrel, MAX 300-LG). The signal of hydrogen ($m/z = 2$) was calibrated with well-known gas mixtures of hydrogen in helium saturated with water.

3. Results and discussion

Fig. 2 shows XRD patterns of the Ti foam (substrate), the homemade Pt-Ru electrode and the TiO₂ modified Pt-Ru electrode. Well defined peaks were observed in all samples. TiO₂ was observed mostly in anatase phase consistent with both the low-treatment temperature (500 °C) and the procedure, which was followed during the preparation of the samples. The formation of solid solutions was excluded since no remarkable shift was observed between the main peaks of Pt, Ru and TiO₂ (Fig. 2). Scherrer's equation (for the peak of Pt at $2\theta = 40.5^\circ$ and $2\theta = 67^\circ$ and of Ru at $2\theta = 38.6^\circ$) was applied to estimate the size of the Pt and Ru crystallite size. The diameters of the crystallites are shown in Table 1. The addition of TiO₂ affects the crystallite size of both Pt and Ru. The decrease of the Pt and Ru crystallite diameter was up to 30% and 36%, respectively. This is in agreement with previous studies in which TiO₂ and especially TiO₂ in the anatase phase could act as a very good substrate for metal dispersion resulting in smaller metal particles and thus in higher active surface area [34–37]. It is worth noting that the specific surface area determined from the adsorption isotherms of nitrogen at -196°C , shown also in Table 1, is almost twice in the case of the TiO₂ modified electrode.

Scanning Electron Microscopy (SEM) was used to explore the surface morphology of the samples and to follow the effect of the TiO₂ loading on the size of the metal particles. Fig. 3(a) and (b) show the comparison of the homemade Pt-Ru and Pt-Ru-TiO₂ electrodes.

Table 1

Crystallite diameters for Pt and Ru according to the XRD patterns and specific surface area for Pt-Ru and Pt-Ru-TiO₂ anodes.

	Pt / nm	Ru / nm	specific surface area / m^2g^{-1}
Pt-Ru	59 ± 3	54	3.8
Pt-Ru-TiO ₂	40 ± 2	34	6.9

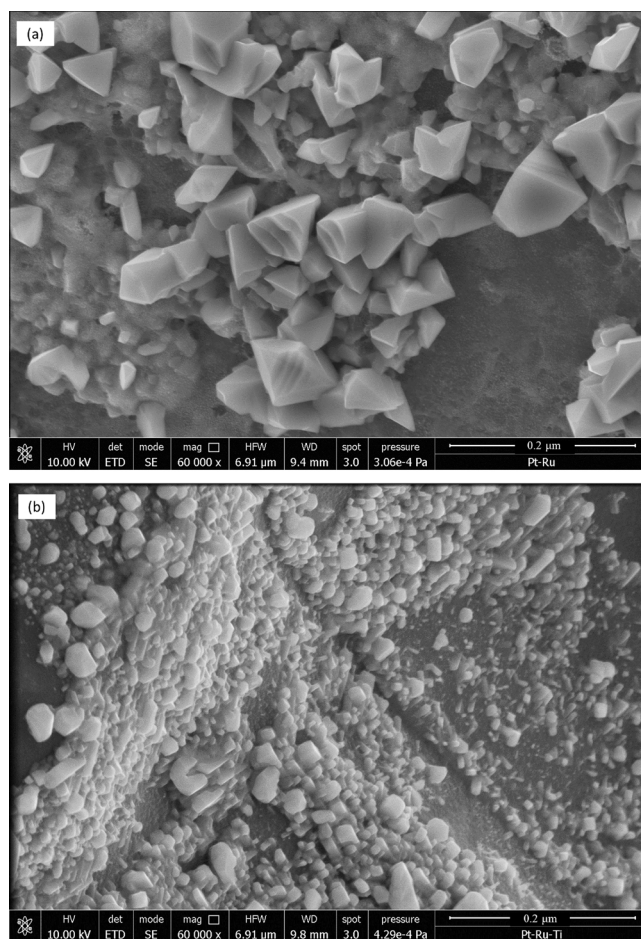


Fig. 3. SEM pictures of the surface of the Pt-Ru (a) and the Pt-Ru-TiO₂ (b) samples.

Although it is difficult to accurately calculate the size of the particles from SEM images, it seems that it doesn't differ significantly from that of XRD patterns. The diameter of the metal particles in the case of the modified TiO₂ electrode is smaller than that of Pt-Ru electrode. According to Fig. 3, the size of the particles from SEM images are 52 ± 10 nm and 30 ± 7 nm for the Pt-Ru and Pt-Ru-TiO₂ samples respectively. It should be mentioned that in the case of the TiO₂ modified sample the metal particles are well dispersed and their size is uniformly distributed on the surface (Fig. 3b).

Fig. 4 shows the effect of methanol concentration on current density for the case of Pt-Ru and Pt-Ru-TiO₂ electrodes at ambient temperature. The concentration of methanol solution was varied between 0.5 M and 3 M. The highest current density for both electrodes was obtained using 3 M methanol solution. The performance of the TiO₂ modified electrode was slightly better in terms of current density since the maximum observed current at 0.85 V was 10% higher than that of Pt-Ru electrode. The concentration of 3 M methanol solution was chosen for the rest of the study.

Fig. 5 shows the effect of temperature on current density. In order to minimize the methanol vaporization and maintain a good electrocatalytic activity, the maximum operating cell temperature was 60 °C below the boiling point of methanol (65 °C) [38]. As shown in Fig. 5(a) and (b), increase of the operating temperature results in a sharp increase of the cell performance. Currents densities up to 400 mA cm^{-2} at 60 °C were observed with the Pt-Ru-TiO₂ anode. Although the Pt-Ru loading for the case of the TiO₂ modified electrode is rather low (0.55 mg cm^{-2}), the current density is comparable or higher in some cases than the values with metal loadings between 1 and 4 mg cm^{-2} .

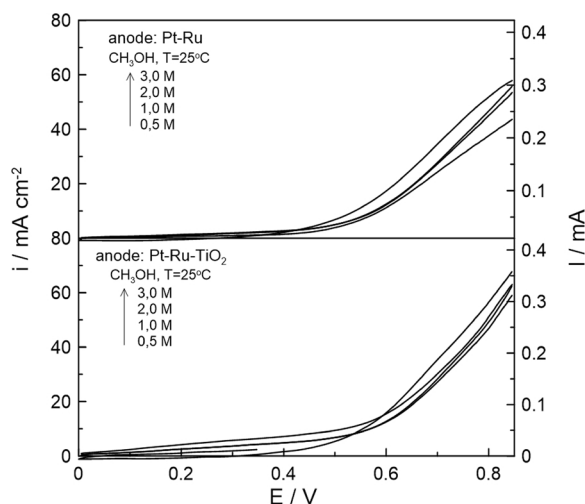


Fig. 4. Effect of concentration on current density for the case of Pt-Ru and Pt-Ru-TiO₂ electrodes. Scan rate 20 mV s⁻¹. T = 25 °C.

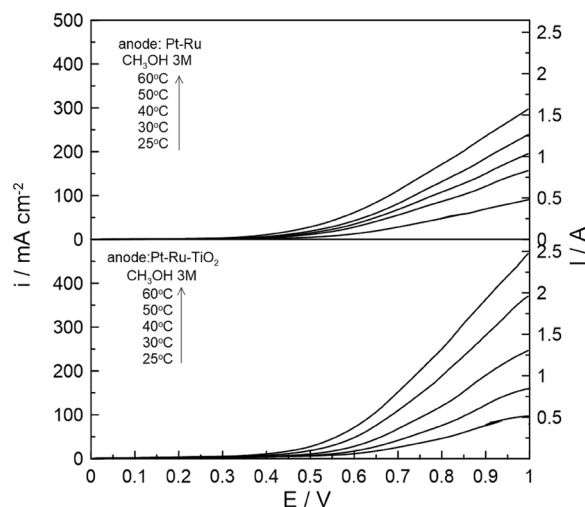


Fig. 5. Effect of cell temperature on current density for methanol solution 3 M for the case of Pt-Ru and Pt-Ru-TiO₂ electrodes. Scan rate: 20 mV s⁻¹.

reported in the literature [8,13,39–45]. We believe that this is due to the better dispersion of the metal catalyst (in the presence of TiO₂), the smaller metal particles and the resulted higher active surface.

In order to have an estimation of the process cost, the energy consumption was calculated for the cases of Pt-Ru and Pt-Ru-TiO₂ electrodes. Fig. 6 shows the electrical energy requirement at three different temperatures at a fixed potential of 1 V. For both cases at 30 °C, the required energy value to generate a certain amount of hydrogen is 27.5 KWh. This value decreases by 1% and 15% for Pt-Ru and Pt-Ru-TiO₂ respectively, as temperature rises from 30 °C to 60 °C. This behavior is attributed mostly to the increase of the membrane conductivity and the kinetics of the reactions. It seems that the second parameter is affected in a pronounced way in the case of the modified electrode.

The cathode of the electrolytic cell was connected with a mass spectrometer (MS) and the hydrogen production rate (r_{H_2}) was measured in real time, parallel with current density for the TiO₂-modified anodic electrode at all temperatures. The recorded cyclic voltammetry (CV) and the mass spectrometric signals (MS) for $m/z = 2$ (hydrogen), $m/z = 44$ (carbon dioxide) and $m/z = 31$ (methanol) are shown in Fig. 7(a) and (b). The observed current density as well as the hydrogen production rate were increased more than 5 times by increasing the temperature from 25 °C to 60 °C. The ratio of the calibrated hydrogen signal ($m/z = 2$) of the MS to the proton flow rate ($I/2F$), which

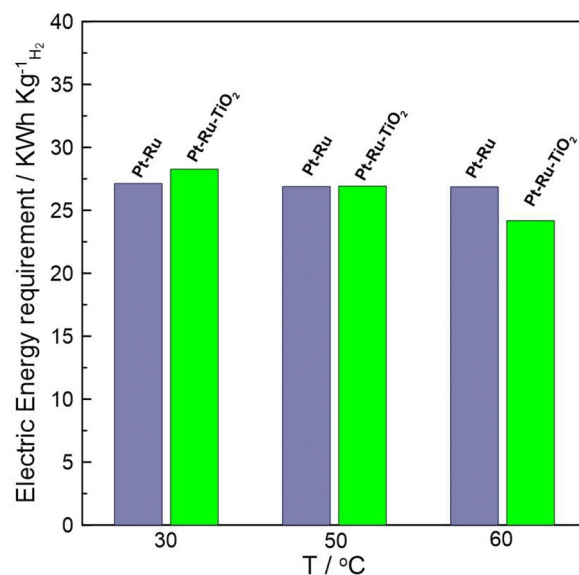


Fig. 6. Electrical energy requirement at three different temperatures for the Pt-Ru and Pt-Ru-TiO₂ electrodes (E = 1 V).

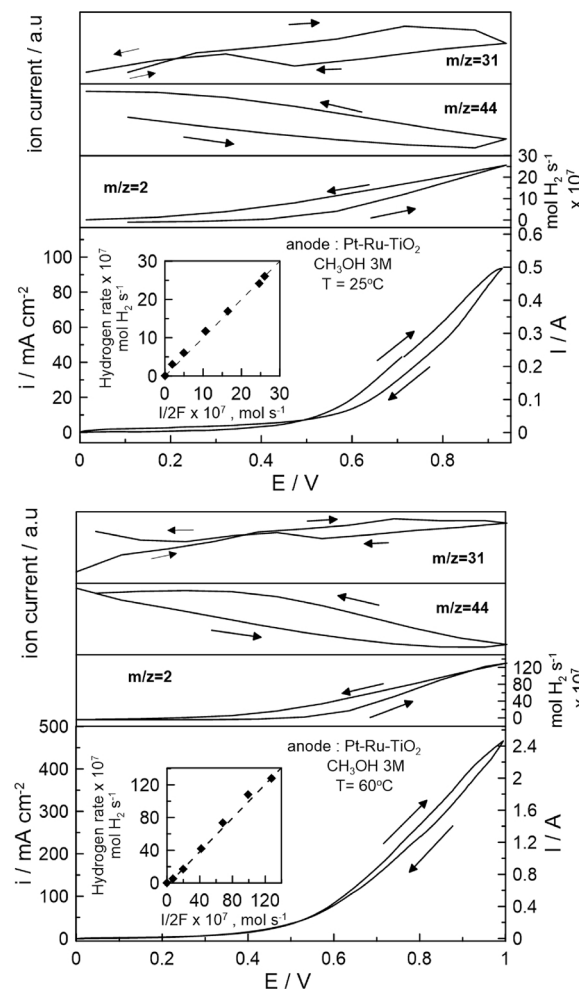


Fig. 7. Simultaneously recorded CV and MS signals for $m/z = 2$, $m/z = 44$ and $m/z = 31$, for the case of the methanol solution 3 M. Operating conditions: temperatures 25 °C (a) and 60 °C (b). Methanol solution 3 M, scan rate = 20 mV s⁻¹.

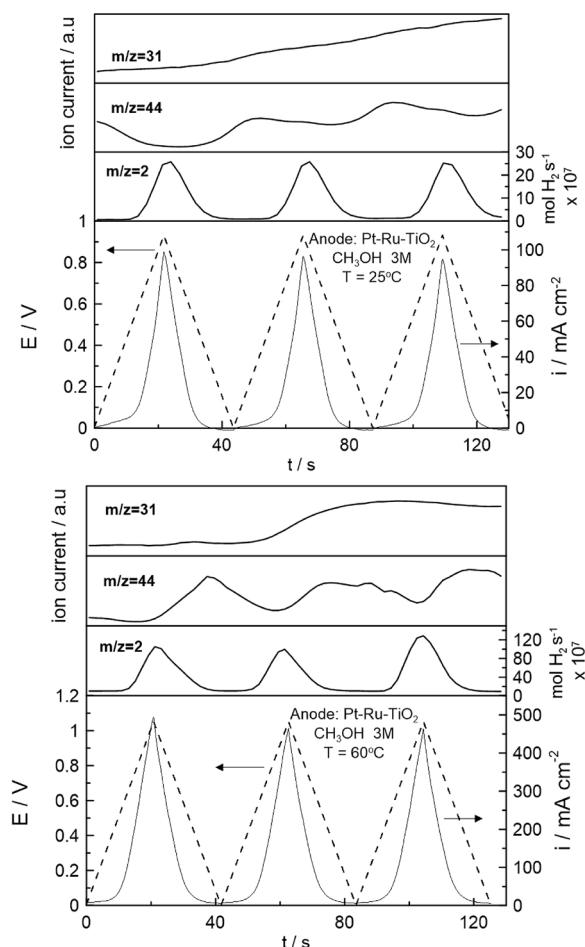


Fig. 8. Effect of applied potential on the current density and the ion currents ($m/z = 31, 44$ and 2) for three consecutive cycles. Operating conditions: temperatures 25°C (a) and 60°C (b). Methanol solution 3 M , scan rate = 20 mV s^{-1} .

provides the efficiency of the process is presented in the inset of Fig. 7. At both temperatures the observed values of this ratio were very close to unity.

Turning our attention to the methanol ($m/z = 31$, Fig. 7), the increased signal with potential and thus with current is a direct proof of methanol crossover. This observation is in agreement with previous reports discussing the drawback of methanol crossover both in methanol electrolyzers and direct methanol fuel cells [37,46–50]. The bigger the current density, the larger the amount of methanol crossover. Interestingly, there is also a variation of the CO_2 signal ($m/z = 44$) at the cathode during cyclic voltammetry. The crossover of CO_2 via different mechanisms has already been discussed in the literature by many research groups [51–54]. Ren et al. reported that CO_2 transport in Nafion membranes is dominated by its transport in the water channels [51]. The MS signals of methanol, carbon dioxide and hydrogen are also shown in Fig. 8 during three consecutive cycles as a function of time. Although methanol seems to be increased monotonously at the cathodic side during time, the migration of CO_2 and its concentration at cathode depends strongly on the current and follows the trend of protons migration with a phase difference. Higher CO_2 signals were observed at low current densities. This behavior could be associated with the higher diffusion coefficient of protons ($\sim 7 \times 10^{-5}\text{ cm}^2/\text{s}$ [55]), during their migration from anode to cathode following a Grotthuss mechanism compared with that of CO_2 ($2.41 \times 10^{-6}\text{ cm}^2/\text{s}$ – $4.61 \times 10^{-6}\text{ cm}^2/\text{s}$, [51]). The amount of CO_2 could be the 2.8%–4.5% of the evolved gas at cathode [12,56].

4. Conclusions

Methanol electro-reforming for hydrogen production was studied in a PEM electrolysis cell. The cell performance was investigated under different operating conditions and by employing Pt-Ru modified with TiO_2 anodes. The current densities achieved with Pt-Ru- TiO_2 electrode were higher than those observed with Pt-Ru. The observed higher electro-catalytic performance of TiO_2 -modified electrode was mainly attributed to the enhanced metal dispersion as well as to the formation of smaller metal particles. The Faradaic efficiency of the TiO_2 -modified electrode at all temperatures was almost 100%. Overall, this study showed that TiO_2 can modify effectively Pt-Ru electrodes by increasing the observed current densities up to 56% (1 V , 60°C) and significantly decrease the noble-metal loading affecting this way the total cost of the process.

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